Journal of Cleaner Production 75 (2014) 1–10

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

Chemicals from biomass – managing greenhouse gas emissions in biorefinery production chains – a review

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ARTICLE INFO

Article history:
Received 19 April 2013
Received in revised form
18 March 2014
Accepted 23 March 2014
Available online 1 April 2014

Keywords:
Biochemical
Biorefinery
Climate impact
Pyrolysis
Hydrothermal liquefaction

ABSTRACT

Growing concerns over the availability and cost of extracting fossil fuel resources have increased interest in renewable resources. Therefore, interest in producing numerous needed chemicals from renewable biomass resources has increased. The focus of this comprehensive review is on managing greenhouse gas emissions (GHG) in biorefinery production chains. To highlight the results of the content analysis an attempt is made to summarize the findings in a climate impact management matrix. In particular, three topics from the matrix are put forward: (1) uncertainties in assessing GHG emissions of feedstock cultivation, harvesting and logistics; (2) found GHG emissions in biorefinery chains; and (3) a short comparative analysis of two potential technologies to improve the GHG and carbon balance of biorefinery operations. In addition, benefits of lignocellulosic biomass, residuals, organic waste and algae are highlighted, sustainability issues of the field are discussed and research gaps are identified. Uncertainties in assessing the sustainability of biofuels supply chains support a more diversified renewable resource base and production of multiple chemicals in biorefinery chains.

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1. Introduction

Growing concerns over the availability and cost of extracting fossil fuel resources have increased interest in renewable resources. On the other hand, reducing anthropogenic greenhouse gas (GHG) emissions is increasingly proposed as one of the key components in achieving global sustainable development goals. Therefore, interest in producing numerous needed chemicals from renewable biomass resources has increased. Renewable biomass resources can be converted to chemicals, and have the potential to replace fossil crude oil as a carbon resource. Production chains starting from renewable biomass resources are considered as 'short-cycle carbon systems' to be more sustainable than 'long-cycle carbon systems' using a fossil fuel resource base. Currently, most chemicals produced from biomass are identified as first and second generation biofuels: bioethanol (largest volumes, 80 billion liters in 2012), biodiesel and biogas (www.ethanolproducer.com). Since biomass is the only renewable carbon resource that could replace fossil ones, the availability and sustainability of these resources is of crucial importance. Biofuels are politically promoted (RED, 2009), and different types of sustainability concerns have arisen including the actual climate impact of biofuels and how extensively they can be utilized without causing significant and irreversible harmful environmental and social impacts. Production of various chemicals from biomass instead of fossil resources requires a paradigm change. The basic question in replacing existing petroleum refinery based production patterns of chemicals with biorefinery processes is the overall sustainability. This change can be studied with impact assessment covering all three pillars of sustainability: economic, social and environmental. Several sets of sustainability indicators and methodologies for estimating the impacts have been proposed (Sacramento-Rivero, 2012). The theoretical sustainability impact assessment framework for a biorefinery chain can be defined on a global, on a regional or on a production site level. On the product or process level, Life Cycle Assessment (LCA) is a methodological tool widely used for estimating and assessing impacts of production systems through their whole life cycle (ISO 2006:14040, ISO 2006:14044). The life cycle of a single site biorefinery consists of feedstock cultivation, harvesting, transportation, intermediate storage, pretreatment, biorefinery operations, product storage, packaging, distribution to customers, use of products, possible recycling and final disposal. The attributional LCA (ALCA), on a cradle to gate basis, reflects the biorefinery production system as it is. Impact allocation cannot be avoided in a biorefinery complex with several product streams. Energy or economic allocation is widely used in published LCAs

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http://dx.doi.org/10.1016/j.jclepro.2014.03.070
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and several options for handling uncertainties are proposed (Finnveden et al., 2009). Striving for sustainable use of resources requires reducing environmental impacts. Especially the net leakage of greenhouse gas emissions needs a serious assessment even when renewable biomass resources are replacing more pollutant fossil fuel derived products. The focus of this paper is on managing GHG emissions in biorefinery chains producing chemicals from biomass. The climate impacts discussed and analyzed here are expressed as greenhouse gas emissions (GHG) attributable to specific chemicals found in the literature. Other related environmental impacts like eutrophication are mostly excluded here. The overall sustainability assessment of biorefinery chains requires, in addition to product level analysis, global and regional analysis that is basically out of the scope of this paper. This review follows, focusing on GHG emissions, the production chain and climate impact matrix described in Section 2. Section 3 covers feedstock issues of cultivation, harvesting, collection, transport and storage, and highlights the uncertainties related to the assessment of GHG emissions attributed to the feedstock supply chain. Section 4 summarizes biorefinery concepts and highlights the GHG emissions of chemicals produced in biorefinery chains. In Section 5 two technologies to improve the GHG balance of biorefinery operations (pyrolysis and hydrothermal liquefaction) are shortly described and compared. Section 6 includes a short discussion including identified gaps in research. Conclusions are presented in Section 7. Abbreviations CO_2 and N_2O are used for carbon dioxide and nitrous oxide.

2. Research methodology

The aim of this review is to summarize the existing research by identifying patterns, themes and issues, and to determine the conceptual content of the field. The search was conducted using databases available from major publishers. The scope covers a total of 340 papers with emphasis on the 238 published in 2011–2013. A short patent search was made for the potential future large scale technologies that were identified in the course of the research.

2.1. Descriptive analysis and category selection

The production chain (Fig. 1) was used for the category selection. A robust classification of publications according to their place in the production chain, supplemented with specific issues of sustainability/LCA, resulted in the topical distribution of publications shown in Fig. 2 and Fig. 3.

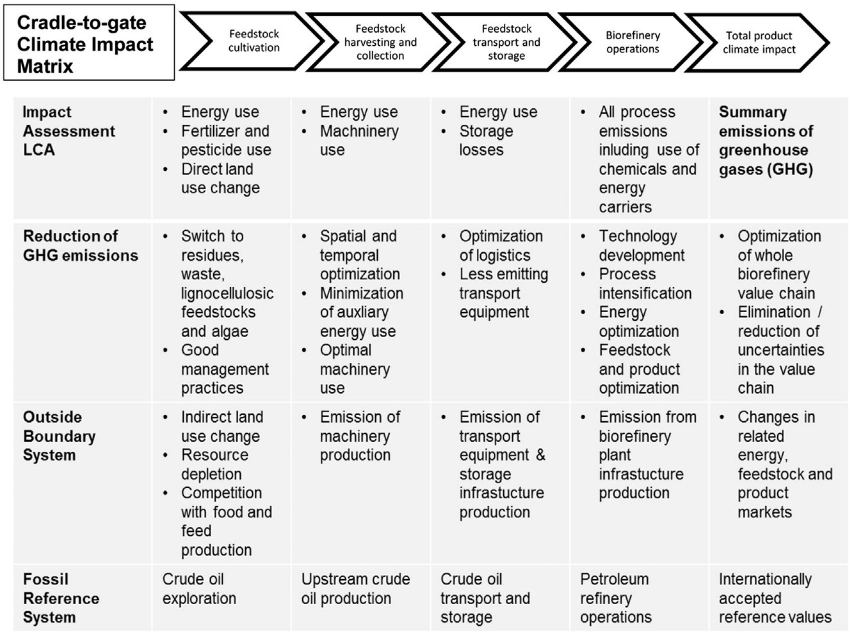
2.2. Material evaluation

The papers studied were analyzed for the identification of relevant issues and interpretations of results. Here an attempt is made to summarize the findings including the system boundary setting in a climate impact management matrix (Fig. 1) elaborated further in the next sections of this paper.

In particular, three topics from the matrix are put forward: (1) uncertainties in assessing GHG emissions of feedstock cultivation, harvesting and logistics; (2) the found GHG emissions of chemicals produced in biorefinery chains; and (3) a comparative analysis of two potential technologies to improve the GHG and carbon balance of biorefinery operations.

3. Feedstock cultivation, harvesting, collection, transport and storage

Renewable feedstock is seldom without GHG emissions when direct and indirect emissions in the supply chain are taken into account. It is notable that lignocellulosic (other than agricultural crops), multiple feedstock (includes at least one lignocellulosic resource) and algae dominate recent research, although feedstock sustainability or LCA studies concentrate on cultivated crops (Fig. 3). When focusing on GHG emissions, an LCA analysis of feedstock supply chain reveals the possibilities to reduce GHG emissions. Biomass feedstock is not uniform in GHG emissions as e.g. a single crude oil field. Therefore, uncertainties in assessing feedstock GHG emissions have raised concerns on the climate impact of bio-based chemicals. Another important issue is how extensively can biomass be utilized without causing significant and



Cradle-to-gate Climate Impact Matrix	Feedstock cultivation	Feedstock harvesting and collection	Feedstock transport and storage	Biorefinery operations	Total product climate impact
Impact Assessment LCA	• Energy use • Fertilizer and pesticide use • Direct land use change	• Energy use • Machninery use	• Energy use • Storage losses	• All process emissions inluding use of chemicals and energy carriers	**Summary emissions of greenhouse gases (GHG)**
Reduction of GHG emissions	• Switch to residues, waste, lignocellulosic feedstocks and algae • Good management practices	• Spatial and temporal optimization • Minimization of auxliary energy use • Optimal machinery use	• Optimization of logistics • Less emitting transport equipment	• Technology development • Process intensification • Energy optimization • Feedstock and product optimization	• Optimization of whole biorefinery value chain • Elimination / reduction of uncertainties in the value chain
Outside Boundary System	• Indirect land use change • Resource depletion • Competition with food and feed production	• Emission of machinery production	• Emission of transport equipment & storage infrastucture production	• Emission from biorefinery plant infrastructure production	• Changes in related energy, feedstock and product markets
Fossil Reference System	Crude oil exploration	Upstream crude oil production	Crude oil transport and storage	Petroleum refinery operations	Internationally accepted reference values

Fig. 1. A matrix for managing greenhouse gas emissions in a biorefinery production chain.

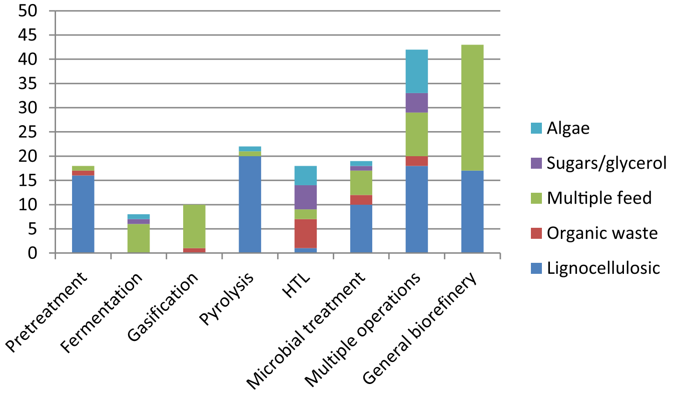


Fig. 2. Technologies dominating recent research with number of publications by feedstock.

irreversible harmful environmental and social impacts. The latter is related to overall land availability and use in general, to competition in land use resources and to the related GHG dynamics.

3.1. *Availability of feedstock*

A multitude of feedstock has been tested for biorefinery applications covering cultivated crops, agricultural waste, forest resources, urban and industrial waste and algae. Studies specifically related to feedstock issues include: bluegreen algae, chlorella vulgaris, citrus waste, dairy manure, food waste, energy crops, EU biomass crops, glycerol (a by-product of vegetable oil esterification), jatropha, lignin, macroalgae, microalgae, miscanthus, municipal waste, organic wastes, rice, seaweed, sugarcane, switchgrass and wheat. Availability of resources seems not to be a short term problem: a conservative estimate on the annual yield of lignocellulosic matter resulting from photosynthesis amounts to 1.3 x109 tons and that of natural oil and fats to 132x106 tons (BREW, 2006). These values might be compared with the world sugar production of 150 x106 tons in the 2008/09 season (Licht, 2009). Rich forest resources account for 89.3% of the total standing biomass (Liu et al., 2012) and are an important feedstock reserve for chemicals. Algae are the primary producers in aquatic ecosystems. An algae plant producing 100,000 bbl lipids per year has a land area requirement of 5–14 km^2 that compares favorably with the 35 km^2 required for similar palm oil production. Microalgae can be produced in industrial fermentation units and do not require similar land reserves (Borowitzka and Moheimani, 2013). Recent studies indicate that the demand for biomass to produce required biofuels and platform chemicals of the petrochemical industry in Europe (EU27) can be covered without significant changes to the current agricultural land use (Bos and Sanders, 2013). However, there is a clear shift from agricultural produce to lignocellulosic feedstock for the production of chemicals (Fig. 2).

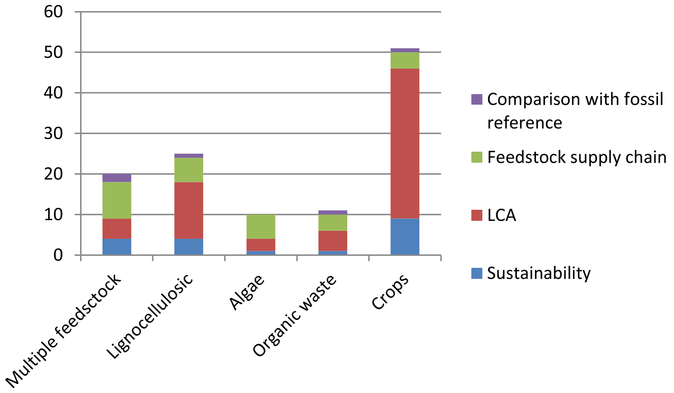


Fig. 3. The distribution of themes by feedstock in 117 sustainability/LCA specific publications.

3.2. *Uncertainties in assessing GHG emissions of feedstock cultivation, harvesting and logistics*

Biomass is a carbon neutral source only when emissions from biomass use are re-absorbed into the re-growth of new biomass. Land use change (LUC) effects and soil N_2O emissions impact the total GHG emission from a biomass feedstock supply chain. Uncertainties of these emissions are recognized, and their influence on final outcomes needs sensitivity analysis. The highest uncertainty relates to the N_2O emissions of cultivation from nitrogen fertilization and to carbon stock changes. Systematic analysis of GHG balances show that agricultural crops (barley, turnip rape) with high probability exceed the GHG emissions of fossil fuels (Koponen et al., 2013). The global warming potential (GWP) of 27 different crops shows considerable variation: the weighted worldwide means of GWP values of the studied crops varied in a wide range. The inclusion of LUC would substantially alter the GWP values (Nemecek et al., 2012). Also, the transport of feedstock has an impact on the GHG emissions. Biomass transport studies could be used as comparative references. The wood pellets transported from Canada to Europe have a total GWP of 295 kg CO_2eq/ton, and 35% of it is attributed to marine transportation (Pa et al., 2012). Similarly, transportation accounted for 27% of the life cycle GWP of South American pulp shipped to Europe (Judl et al., 2011). The impact of transport could be reduced by small scale production without loss of GHG benefits or by reducing the transport volume by decentralized pyrolysis plants that convert e.g. wood chips into liquid form (Haro et al., 2013). Overall, the benefits of decentralized production depend on the size of the territory wherefrom the raw material is collected (Iglesias et al., 2012). Conclusively, in addition to the feedstock, the transport type and distance will define the impact of logistics on the overall GHG emission in a biorefinery production chain. An overview of GHG emissions related to woody biomass is presented by Liu et al. (2012).

3.3. *Composition of feedstock*

There is a considerable diversity of feedstock by composition. Chemical feedstock categories are carbohydrates, lipids, proteins and lignocellulosic (LC) materials. Some, such as corn, are highly developed, while others, such as LC and algae, are in an earlier stage of development. Carbohydrates of corn, sugarcane, grains and potatoes, and lipids of edible oils as valuable food and feed resources are not the best sustainable options for biorefineries. The composition of LC feedstock is documented among others by Menon and Rao (2012). After cellulose, lignin is abundantly available, and being an aromatic biopolymer makes a valuable renewable source for aromatics. The amount of recoverable lignin in different resources varies widely, ranging from 3% in corn cobs to 27% in oak (Kaylen et al., 2000). In addition, lignin and lignin containing residues are large side-streams (currently burned for heat and electricity) from the pulp and paper industry and biorefineries producing bioethanol from LC materials.

3.4. *Reduction of GHG emissions of feedstock supply chain*

Considerably high GHG emissions of many cultivated crops and uncertainties in their determination support the switch to residues, waste, LC feedstock and algae. The importance of spatial and temporal optimization of feedstock cultivation, harvesting and collection, as well as that of logistics, is demonstrated for cellulosic supply chains (You et al., 2012). The fast recycle and high production rates of algae compared to crops, grasses and forest resources (Liu et al., 2012) increase the climate benefit of this resource. Good management practices, minimization of auxiliary energy use, optimal machinery use and use of less emitting transport equipment are eligible options also for the management of GHG emissions in feedstock supply chains of biorefineries. The overall assessment of sustainability is complicated by the fact that the carbon footprint of cultivation differs significantly among locations (Gan et al., 2012). The cultivation emissions of N_2O can be responsible for more than 50% of the contribution to GHG emissions (Ekman and Börjesson, 2011). Harmonized calculation principles with emission saving probabilities are proposed to make the results more credible (Koponen et al., 2013).

3.5. Issues outside the boundary system

Several issues outside the framework of direct climate impact assessment of a feedstock supply chain impact the overall sustainability of a biorefinery production chain. These include indirect land use changes (ILUC) that are outside normal ALCA, resource depletion and competition with food and feed production. The world total surface area is 13,400 million hectares (Mha) with forest covering about 4000 Mha and arable agricultural land 1500 Mha. The total agricultural potential is estimated at 5000 Mha (FAO, 2010). This and maximum photosynthesis output define the sustainability framework for future generations to utilize biomass and to benefit from agriculture for food and feed production. Therefore, biorefineries need to select their feedstock for chemicals production avoiding direct competition with food and next generation biofuel production. Conclusively, forest and agricultural residues, industrial and urban side and waste streams, and algae are considered more suitable options.

3.6. Comparison with the fossil reference system

Compared to petroleum resources, biomass needs to be harvested, and collection is sometimes possible only in a specific season. In addition, the lower volume density and heat content of biomass resources increase the transport volumes. Therefore, the overall GHG emissions of biomass supply chains need to be included when comparing the emissions of biorefinery production chains with the corresponding emissions of producing e.g. petrochemicals. Evaluating 16 bioenergy crops, Brehmer et al. (2009) concluded that the highest potential of biomass to replace fossil resources is in the petrochemical industry. In contrast to petroleum resources, all biomass components contain high percentages of oxygen (Nzihou et al., 2012). The molecular difference between fossil products and biomass derived ones is shown in Table 3.

4. Biorefinery operations and GHG emissions from biorefinery production chains

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass (NREL, 2010). Biorefineries can use a variety of biomass materials and through a series of conversion and separation steps yield bulk and specialty chemicals and materials. GHG emission is one of the indicators that describe the potential sustainability impact of a production chain. Here GHG emissions are defined as the overall “cradle-to-gate” carbon dioxide equivalent emission (CO_2eq) per unit of chemical produced.

4.1. Biorefinery concepts and operations

Biorefinery facilities can be classified by several categories either by feedstock materials, resulting products, technologies utilized or a combination of all three categories. In fact, how these categories are combined forms the complexity of integrated biorefineries. Biomass feedstock categories by key chemical composition are carbohydrates, lipids, proteins and lignocellulosic materials. Resulting product categories are biofuels, chemicals and their intermediates, biogas, electricity and heat. A variety of technologies and unit operations, including fermentation, gasification, pyrolysis, hydrothermal liquefaction, hydrogenation, hydrothermolysis, oxidation and hydrodeoxygenation, are available or under development for biorefineries. Research on different biorefinery technologies is increasing. The number of identified publications doubled from 2011 to 2012. Key technologies found and their distribution by feedstock is shown in Fig. 2. General biorefinery publications (Fig. 2) relate to overall optimization and techno-economic assessment of different biorefinery concepts. Lignocellulosic and multiple feedstock dominate in publications, reflecting the need to find suitable feedstock to replace agricultural and energy crops in future biorefineries. Mature technologies for treating sugarcane/corn and vegetable oils cover only 6% of recent publications on biorefinery technologies.

All concepts identify a varying palette of products covering a whole range of potential production volumes and market values. Depending on the geographic location and on feedstock available, the products, selected technologies and sequence of unit operations differ to obtain the highest profit for the biorefinery. Different sets of key chemicals have been proposed. Table 1 shows typical bulk chemicals and the basic compounds of the current fossil petrochemical industry. Biofuel fractions of gasoline and diesel are not included in the list. The evolution of biorefinery technologies narrows the cap between petrochemicals and chemicals produced from biomass. The production of aromatics from lignocellulosic

Table 1
Typical chemicals from biomass produced with different technologies.

Carbon atoms	Fermentation	Multiple technologies	Woody biomass refinery	Fossil reference system
C1	Methane (biogas) Ethanol	Methane Methanol	Methanol	Methane
C2	Acetic acid Lactic acid	Ethanol Ethene	Ethanol	
C3	Glycerol 1.3-propanediol Fumaric acid	Propene Glycerol Propane-1.2-diol	Acetic acid Lactic acid Acetone	Ethene Propene
C4	Succinic acid 1-butanol 1.4-butanediol Aspartic acid Furfural	Butene 1.3-Butadiene iso-Butanol	Succinic acid Butanol	Butene 1.3-Butadiene
C5	1.2.4-butanetriol Levulinic acid Citric acid	Ethylene glycol	Furfural Levulinic acid Itaconic acid Benzene	
C6	Lysine Glutamic acid 5-hydroxymethylfurfural	Benzene Dimethylfuran	Benzene	Benzene
Others	Amino acids Vitamins Biopolymers Industrial enzymes Antibiotics	Toluene o,p,m-Xylene Hydrogen Proteins Amino acids	Toluene o,p,m-Xylene Hydrogen Xylitol	Toluene o,p,m-Xylene Hydrogen

Sources: BREW, 2006; Bos and Sanders, 2013; Liu et al., 2012, Posada et al., 2013; Wang et al., 2013; Yao and Tang, 2013.

Table 2
GHG emissions of biorefinery production chains.

Feedstock	Product	Yield	CO_2eq. emissions$^{7)}$ kg CO_2/kg product	Carbon loss%	Reference
Soybean	VOME$^{1)}$	17.7%	4.0	n.a.	Panichelli et al., 2009
Oil palm	Ref. palm oil	n.a.	2.16–2.60	n.a.	Schmidt 2010
Rapeseed	Ref. rapes oil	n.a.	2.22–17.1	n.a.	Schmidt 2010
Rapeseed	FAME	n.a.	1.90–3.42	n.a.	Pehnelt and Vietze, 2012
Oil palm	FAME/HVO	n.a.	1.59–6.67	n.a.	Soimakallio and K 2011
Animal fat	HVO	n.a.	0.47–0.75	n.a.	Soimakallio and K 2011
Wheat	Ethanol	29.4%	0.965	n.a.	Misailidis et al., 2009
Grain	Ethanol	n.a.	0–20.70	n.a.	Soimakallio and K 2011
Sugarcane	Ethanol	n.a.	0–8.66	n.a.	Soimakallio and K 2011
Cellulosic	Ethanol	n.a.	0–1.76	n.a	Soimakallio and K 2011
Corn stover	Ethanol	0.37 l/kg feed	n.a.	71%	Humbird et al., 2011
Switchgrass	Ethanol	30%	0.473	n.a.	Cherubini and J 2010
Waste	Ethanol	n.a.	0.28–4.03	n.a.	Soimakallio and K 2011
Algae	Biodiesel	<30%	5.654	n.a.	Sander and Murthy, 2010
LC Biomass	Synfuel	50%	1.15	>30%	Nzihou et al., 2012
Wood	Liquid fuel	n.a.	0–3.10	n.a	Soimakallio and K 2011
Switchgrass	Phenol$^{2)}$	0.5%	0.59	n.a.	Cherubini and J 2010
Glucose$^{3)}$	Methanol	n.a.	1.124	59%	Bludowsky and A 2009
Wheat	Arabinoxylan$^{6)}$	0.64%.	0.175	n.a.	Misailidis et al., 2009
Bioethanol	PVC$^{8)}$	n.a.	0	n.a.	Alvarenga et al., 2013
Biomass	Chemical pulp	n.a.	0.441–0.554	n.a.	Judl et al., 2011
Wood	Imported pellets$^{4)}$	0.295			Pa et al., 2012
Fossil fuel reference values, recalculated from kg CO_2eq/1000 MJ fuel to kg CO_2eq/kg fuel using LHV$^{5)}$					
Fossil	Gasoline	3.91–5.17			GREET 2008
Fossil	Diesel	3.57–3.59			RED 2009
Fossil	Hydrogen	12.98			GREET 2008
Fossil	Natural gas	3.30			GREET 2008

Notes. 1) VOME = vegetable oil methyl ester, produced in Argentina and consumed as B100 biodiesel in Switzerland, 2) By-product of ethanol production, GWP calculated through energy allocation by the author of this review, 3) Models sugars of LC biomass, 4) Pellets from Canada to Netherlands by marine transport, 5) LHV = lower heating value from Biomass Energy Data Book-2011-http://cta.ornl.gov/bedb, 6) CO_2eq emission calculated using economic allocation by the author of this review, 7) kg CO_2eq/kg emission value refers to the product derived from the feedstock shown in the corresponding line. All reported negative emission values are expressed as 0, 8) PVC = polyvinyl chloride, assumed to be a carbon sink (fossil PVC's GHG emission is 1.52 kg CO_2eq/kg).

biomass is still without commercial breakthrough although research on lignin utilization is progressing. At present the world chemical industry produces about 300 Mt/a petrochemicals (Sanders et al., 2012), and at least an equal amount of similar chemicals would have to be produced from biomass.

The amount and type of biomass required to produce a replacement for petrochemicals depend on the selected technologies and on the mass efficiency of the selected chemical route, e.g. ethene produced from sugars via ethanol can have a maximum theoretical carbon efficiency of 30% even if ethanol to ethane conversion would be with 100% efficiency. A multi-criteria sustainability screening assessed potential chemicals produced from bioethanol and found that 1.3-butadiene and diethylether are the most promising derivatives followed by ethylene, propylene, acetaldehyde, ethylene-oxide and ethyl acetate. Iso-butylene, hydrogen, n-butanol, acetic acid and especially acetone were not considered attractive options for bioethanol conversion (Posada et al., 2013).

What is the most attractive industrial domain for future biorefineries? Based on historical data, Bennett and Pearson (2009) concluded that the established links between fuel and bulk chemical production and the direct competition between different uses for biomass resources could have significant influences on whether biorefineries emerge primarily from the chemical, fuels or forestry industry. The situation has developed fast and several commercial next generation biorefineries are already in operation.

Commercial biorefineries in Finland have emerged in the domains of the energy, fuel and forestry industry: The St1 energy company utilizes food industry waste as feedstock and operates 5 bioethanol/biogas plants with a total annual E85 gasoline capacity of 5000 tons. The company is also designing a lignocellulosic, sawdust based bioethanol plant with an annual capacity of 10 million liters. The power company Fortum is commissioning a fluidized bed fast pyrolysis oil production based on woody biomass with an annual capacity of 50,000 tons. Neste Oil's global production of biodiesel from lipids is 2 million tons per year, and their NExBTL technology is suitable for chemicals production. Pulp and paper producer UPM is commissioning a 100,000 t/a biodiesel plant utilizing crude tall oil as a feedstock. In addition, the company is planning a woody biorefinery based on gasification + FT technology in Strasbourg, France. Luleå University of Technology in Sweden owns and operates the former Chemrec pilot plant of black liquor gasification producing methanol and dimethylether (DME). The technology has not been commercialized in a full scale plant. The 120-year-old Borregaard biorefinery in Norway is currently producing cellulose, ethanol, lignin derivatives and vanillin. Similar diversification between fuel, chemical and forestry companies is happening in the USA, where over ten cellulosic biorefinery projects employing six different pathways are expected to begin operations by 2014.

4.2. *GHG emissions of chemicals produced in biorefinery chains*

The overall GHG emissions from biorefinery production chains can be assessed by applying a “cradle-to-gate” LCA. These emissions can be divided into originating from feedstock, transportation to site and from actual refinery emissions (Fig. 1). Depending on the boundary conditions and system limitations the results vary widely and are expressed in a multitude of different units. A thermochemical conversion process for woody biomass was benchmarked for an ethanol process (Dutta et al., 2011). Fig. 3 indicates that research on sustainability and LCA concentrates on cultivated crops,

Table 3
Empirical H/C and O/C molar ratios of various biomass and products.

Feedstock/product	Molar H/C	Molar O/C	Reference
Biomass, average	1.50	0.67	Nzihou et al., 2012
Biomass, average	1.40	0.60	Mohan et al., 2006
Sewage sludge	1.65	0.53	Nzihou et al., 2012
Wheat straw	1.47	0.70	Nzihou et al., 2012
Almond shells	1.46	0.62	Nzihou et al., 2012
Bagasse	1.43	0.64	Nzihou et al., 2012
Demolition wood	1.27	0.55	Nzihou et al., 2012
Biodiesel B100	1.87	0.11	Anitescu, Bruno, 2012
Biodiesel B20	1.94	0.02	Anitescu, Bruno, 2012
Bioethanol	3.00	0.51	Anitescu, Bruno, 2012
Bagasse oil	1.42	0.52	Mohan et al., 2006
Sesam stalk oil	1.55	0.36	Mohan et al., 2006
Microalgae oil	1.69	0.23	Mohan et al., 2006
Hybrid poplar oil	1.32	0.47	Mohan et al., 2006
Wood bio-oil, average	1.34	0.50	Mohan et al., 2006
Turkish red pine oil	1.38	0.37	Mohan et al., 2006
Fossil gasoline	1.95	0.00	Anitescu, Bruno, 2012
Fossil diesel	1.95	0.00	Anitescu, Bruno, 2012
Fossil heavy fuel oil	1.55	0.01	Mohan et al., 2006

reflecting concerns that increasing production of bioethanol and biodiesel competes on agricultural land with food and feed production.

4.2.1. Units used in GHG balances

The papers reviewed reported GHG balances in several functional units (FU). Although all results were reported as GHG emissions, the variable overall metrics and system boundaries were not comparable, making general conclusions difficult. The proposed GHG management matrix would benefit from harmonized metrics and make different feedstock and technological approaches more comparable. Selecting the FU of the assessment as 1 ton of feedstock for the feedstock part of the matrix, and as 1 ton of product for the biorefinery (BF) part of the matrix in accordance with the normal practice in the chemical industry, would allow the calculation of summary emissions of a BF production chain in a uniform metrics as described by Eq. (1):

$$E_{\mathrm{Total}} = E_{\mathrm{Feedstock}} + E_{\mathrm{Logistics}} + E_{\mathrm{BF}} \tag{1}$$

and the amount of GHG emissions in respective components is quantified by Eqs. (2) and (3).

$$E_j = C_F \times \sum\nolimits_{i=1}^{n} e_{j,i} \;\; (i = 1, 2, 3, \ldots n) \tag{2}$$

where C_F is the mass fraction of feedstock required; and $e_{j,I}$ is the cultivation or logistics emissions of a feedstock (i = emission source i.e. N_2O, land use change, GHG emission from cultivation equipment, emissions from harvesting, collection, transport…) and

$$E_{\mathrm{BF}} = \sum\nolimits_{i=1}^{n} e_{\mathrm{bf},i} \times C_{B,i} \;\; (i = 1, 2, 3, \ldots n) \tag{3}$$

where $C_{B,i}$ is the fraction of emission (i) allocated for the production of a single product; and $e_{\mathrm{bf,i}}$ is the biorefinery emission (i) per ton of total production *(i = emissions from energy carriers, auxiliary materials, power consumption, process emissions…)*. When fractional allocation by mass is not possible in a multiproduct chain, energy or economic allocation would be necessary.

4.2.2. Variations in methods of LCA

In terms of methods, part of the papers reviewed simplify the assessment, e.g. for convenience only CO_2 emissions are counted as GHG emissions, and the fossil energy reference system is simplified. Also, the life cycle stages included in the assessments varied, as did the system boundaries. The LUC, ILUC and N_2O emissions from fertilizer use were often left outside the system boundary definition. By defining the final product as a carbon sink, high overall emissions are compensated to zero or a negative value (Alvarenga et al., 2013). The use of average or medium values without including the full variation range of a parameter does not always give the full picture of the climate impact. Uncertainty and sensibility analyses are important for evaluating the GHG emissions of feedstock supply chains, as discussed in Section 3.2.

4.2.3. GHG emissions of chemicals produced from biomass

The GHG emissions of biomass based production chains as “climate neutral” were seldom contested prior to 2005 (Mohan et al., 2006). The GHG balances of different biofuels originating from various raw materials and different regions based on 25 studies show the opposite with considerable variations in results (Soimakallio and Koponen, 2011). In particular, rapeseed biodiesel and soybean-based methyl ester (VOME) showed high GHG emissions (Table 2). Also LCAs of bioethanol systems showed wide variations (von Blottnitz and Curran, 2007). The GHG emissions strongly depend on the life cycle stages included. The uncertainties and relatively high GHG emissions of first generation biofuel production chains support the switch to producing more chemicals from biomass, replacing petrochemicals.

The chemical industry usually reports their GHG emissions as kg CO_2eq/kg of product. The climate impact of chemicals expressed as CO_2eq emissions is shown in Table 2. The values that were originally reported in g CO_2/MJ fuel were recalculated to kg CO_2/kg product for clarity, using higher heating values (HHV) of corresponding bioproducts (GREET 2010 http://greet.es.anl.gov). The HHV values give approximately 6.5% lower CO_2eq emissions per kg of product than those calculated with lower heating values (LHV). The overall magnitude of emission levels (Table 2) indicates the current understanding of the climate impact of biorefinery production chains. Compared to the fossil reference values, bioethanol and VOME in particular show considerable variation. The results point out not only the wide variation of feedstock cultivation emissions, but also differences between numerous LCA methods generating conflicting results.

The LCAs of a single chemical outside biofuels are practically missing: in addition to biomethane, bioethanol, PVC and polyitaconic acid, only the climate impact of methanol produced from bio-syngas could be identified from the papers selected for this review. Bludowsky and Agar (2009) compared different bio-syngas to methanol routes. The carbon ‘loss’ is mainly a consequence of the fact that water must be added in the reforming step to attain the syngas ratio of C:H:O = 1:4:1 needed for methanol. The oxygen thus introduced must be eliminated as CO_2. A major disadvantage of the synfuel gasification process is that even if external heat is available, 30% of the feed carbon is lost, representing 1.15 kg CO_2 per kg product. Methanol is itself a feedstock for a whole series of further chemicals. The largest amounts are used in the manufacture of formaldehyde (35%), MTBE (9%) and acetic acid (9%). Misailidis et al. (2009) investigated the economic feasibility of co-producing an arabinoxylan (AX) product with ethanol from wheat, reporting the GHG emission for pure ethanol. By using economic allocation, the author of the current review estimates that the share of CO_2 emissions of coproduced AX would amount to 0.175 tons CO_2 per one ton of AX (considered as a potential, natural replacement for other viscosity-enhancing ingredients used in the food industry). Similarly, using energy allocation, the GHG emission of coproduced phenols would be 0.59 tCO_2eq/t phenols, and the value would double if the soil C sequestration benefit was omitted (Cherubini and Jungmeier, 2010). A carbon balance for ethanol production indicates that over 96% of all carbon in the process enters in the biomass feed, and that 29% of carbon atoms leave as ethanol. Major exit points for the balance of carbon (accounting for 66%) are the combustor stack and scrubber vent. The ethanol yield was 76% of the theoretical one (Humbird et al., 2011). This indicates the current low carbon efficiency of bioethanol production chains.

4.3. Reduction of GHG emissions in biorefinery production chains

The low carbon efficiency of current biorefinery operations is directly linked to the relatively high GHG emissions reported. Technology development of multiple operations, process intensification, energy optimization, feedstock and product optimization, optimization of value chain and elimination/reduction of uncertainties in the value chain are all issues identified for the reduction of GHG emissions (Sanders et al., 2012). The optimal solution depends highly on the plant location, overall plant configuration and technology available (Moriizumi et al., 2012). Not properly selected technology can destroy the assumed benefits of algae. New, more economic extraction processes for microalgae show better net GHG emissions (Ferreira et al., 2013). Innovative approaches that combine technologies outside the actual process operation can give considerable benefits. By using concentrated solar systems the area of land required for growing biomass can be reduced to one half of that needed for a standard gasification system. If also hydrogen is generated by solar means, the figure becomes one third (Nzihou et al., 2012).

4.4. Issues outside the system boundary

Changes in related energy, feedstock and product markets have an impact to the sustainability of biorefinery production chains. Shifting markets and increased global competition are drivers that grow the interest of the forest sector to invest into new biorefinery technologies (Hämäläinen et al., 2011). The use of biomass for electricity and fuels is not necessarily enabling optimal GHG savings. Often the production of chemicals and materials offers higher savings than bioenergy per kg feedstock as well as per hectare of cultivated land (Hermann et al., 2011). Policies to incentivize efficient GHG reductions that secure sustainable use of biomass without compromising food and feed production are needed. The energy use and biofuel production from agricultural residues are often competing options (Delivand et al., 2012). Conclusively, it is sometimes difficult even at a country level to assess the sustainability of different options for the utilization of one and the same biomass.

4.5. Comparison with a fossil reference system

Comparative LCAs are a tool for assessing the sustainability of the change from fossil resources to renewable biomass. A biorefinery concept based on switchgrass was compared with a fossil reference system producing the same products/services. The results showed that GHG emissions are decreased by 79%, and about 80% of non-renewable energy is saved, even if only about 33.6% of the original energy content of the feedstock is found in the final products (Cherubini and Jungmeier, 2010). The allocation of GHG emissions between different products is not fully solved. Even in complex fossil fuel refinery systems, the allocation of energy content and GHG emissions between products is not without problems. Also a general lack of methods to compare petroleum and wood-based products is recognized (Clancy et al., 2013).

Two other issues that require a solution are molecular differences between fossil and biobased feedstock and products, and the lower carbon efficiency of current biorefineries. In contrast to fossil fuels, all biomass components contain high percentages of oxygen, with e.g. cellulose containing about 50–52 wt% oxygen and correspondingly lignin 28–33 wt% oxygen (Nzihou et al., 2012). Molar H/C and O/C ratios, calculated on the basis of empirical data of elemental analysis (Table 3) are important. The further the ratios are from fossil reference values the more reactions (e.g. hydrotreatment, hydrodeoxygenation) are required to find pathways to produce the same type of products as current petroleum refineries do today. Higher oxygen to carbon ratios offers also new possibilities to produce oxygen containing molecules like butanol, methyltetrahydrofuran (MTHF) and ethers (Melin and Hurme, 2010). Oxygen-rich monomers like carboxylic acids (lactic acid, succinic acid, itaconic acid and levulinic acid) are gaining interest as biopolymers (Yao and Tang, 2013). Also several other chemical routes to utilize succinic acid are recognized (Wang et al., 2013). The effective conversion of various biomass resources, with the over 90.6% carbon and energy efficiency as reached in modern petroleum refineries, is an unsolved challenge. As stated earlier, the carbon efficiency of fermentation bioethanol is about 30% and that of biomass gasification technology less than 40%. The conversion efficiencies of pyrolysis and hydrothermal liquefaction (HTL) are expected to reach 75 wt% and 67 wt% (Suali and Sarbatly, 2012). To narrow the gap between the production of petrochemicals and their biobased counterparts, research on valorization of products and on finding optimal biorefinery concepts is expanding rapidly (Fischler, 2012). The aromatic chemicals isolated from lignin could be used by the conventional petrochemical processes, which convert bulk aromatics into nylons, resins, polymers and other compounds. The aromatic building blocks of lignin; benzene, toluene and xylene (BTX) dominate the research (Cherubini and Strømman, 2011).

5. Two potential technologies to improve the GHG and carbon balance

The low carbon efficiency of current fermentation technologies and considerable stack emissions of CO_2 from generally energy efficient gasification technologies could be overcome with biorefinery configurations that involve new technologies. Pyrolysis and HTL have the potential to improve the overall GHG and carbon balance of biorefinery production chains. It can be argued that the rest of the feedstock carbon is effectively used for heat and power generation inside the biorefinery, and that the overall GHG emissions (mainly as stack CO_2) would be sequestrated in the biomass cycle or could be captured otherwise (e.g. CCS). Taking into account the uncertainties of GHG emissions in the feedstock supply chain and land use restrictions, it is better to improve the carbon efficiency of operations.

5.1. Pyrolysis of biomass

Pyrolysis means degradation at high temperature in the absence of oxygen or air. Chemically, pyrolysis of cellulosic biomass at 500–600 °C can be expressed in a simplified way as follows:

$$(C_6H_{12}O_6)_m \rightarrow \text{gas}\ (H_2 + CO + CO_2 + CH_4 + \ldots + C_5H_{12}) + \text{liquid}\ (H_2O + \ldots + CH_3OH + CH_3COOH + \ldots) + \text{char}\ (C)$$

Hemicellulose and lignin form more complex liquid compounds including phenols and other aromatic compounds. Pyrolysis is no new technology and has been used for hundreds of years to produce e.g. tar from pine and spruce in a slow process. Typical pretreatment methods prior to actual pyrolysis are: milling and drying for woody biomass, hydrolysis, aquathermolysis and torrefaction for wet or high sugar/lipid containing biomass depending on the composition of the desired process streams (Perez-Cantu et al., 2013). Lignin recovery from pulp mill streams needs special technology. The LignoBoost (www.metso.com) process consists of precipitation of lignin from the black liquor vapor by lowering the pH with CO_2, dewatering of slurry using a filter press, redissolving the lignin in spent wash water and acid, final dewatering and washing with acidified wash water, to produce virtually pure lignin cakes. The first commercial unit with a 75 t/d capacity was commissioned by Domtar, USA in April 2013. New commercial large scale pyrolysis units are usually fluidized bed solutions, and recent developments show encouraging results (Solantausta et al., 2012). Typically, high pressures (100–200 bar) and temperatures (300–450 °C) are required to convert lignin into low molecular weight compounds in good yield with an overall carbon efficiency of 75 wt %. Catalysts enhance the quality of pyrolysis oil (Guo et al., 2012). The extraction of specific chemicals, upgrading of the complex pyrolysis oil mixture to usable and valuable bulk products, are difficult tasks (Vispute et al., 2010). Recovery of lignin and acetic acid from pulp mills are considered more viable alternatives than direct dry wood distillation and pyrolysis (Pettersson and Harvey, 2012). The commercialization of pyrolysis technology is in its pivotal phase: the technology has a wide patent coverage owned by UOP/Honeywell, the required fast fluidized bed installations are available from several producers, and the first large (50,000 t/a) scale facility for woody biomass is under commissioning by Fortum, Finland. The product is scheduled to replace heavy fuel oil but can, in the future, be utilized for the production of chemicals (oxygenated compounds like sugars, acids, furans, phenols, aldehydes, ketones and water insoluble lignin derived oligomers) when separation technologies become more developed.

5.2. Hydrothermal liquefaction of biomass (HTL)

HTL is a technique for obtaining clean bio-oil and water insoluble fractions from biomass in the presence of a solvent or water. HTL of biomass has been studied for a little over 40 years. Various biomass resources require different types of pretreatment. Even though the HTL process tolerates up to 65% water content of the feedstock, the transport distance usually stipulates how much pressing, caking, and water reduction is required prior to the HTL unit. Process conditions, including final liquefaction temperature, residence times, rate of biomass heating, size of biomass particles, type of solvent media, hydrogen donor solvents and catalysts, are important for the bio-oil yield and quality of the product (Akhtar and Amin, 2011). Several HTL studies are focused on different algae (Jena et al., 2011). The high lipid content of algae produces bio-oil with high energy content that is comparable with fossil reference values. Municipal lipid containing waste and swine manure are both abundantly available and sources of methane if landfilled or stored in waste ponds. The technology is currently being tested on a pilot scale at Aarhus University, Denmark, and has the following benefits: the process accepts sewage sludge, manure, wood, compost and plant material along with waste from households, meat factories, dairy production and similar industries; the crude bio-oil has high heating values of approximately 35–39 MJ/kg on a dry ash free basis; the process consumes approximately 10–15% of the energy in the feedstock biomass, yielding an energy efficiency of 85–90%; the crude bio-oil has very low oxygen, sulfur and water content; the process recovers more than 70% of the feedstock carbon content; and the resulting bio-oil is storage stable and has comparatively low upgrading requirements.

5.3. Comparison of pyrolysis and hydrothermal liquefaction (HTL) of biomass

Both pyrolysis and HTL can virtually accept any form of biomass. In practice, woody biomass is most often subjected to pyrolysis and wet biomass, like algae and manure, has been more widely treated with HTL. Both processes produce crude pyrolysis oil, pyrolysis gas and solid residues (Table 4). Pyrolysis gas usually contains a mixture of hydrogen, methane and other hydrocarbons (up to C5), carbon monoxide and carbon dioxide that can be further processed to fuels and chemicals or utilized as an energy stream in the process. From HTL the gaseous product is methane gas. Solid residues can be utilized further in agricultural or forest soil improvement either as such or as ash. Crude bio-oils require further processing to reach the physical properties required from final chemical products.

Both technologies are expensive in large scale applications. A suitable cost reference could be a fluid catalytic cracking (FCC) unit of a petroleum refinery or a large bubbling fluidized bed (BFB) boiler. Several technological and economic issues require solutions before pyrolysis and HTL of biomass can be considered fully commercialized for the production of chemicals.

6. Discussion

The growing global population and its need for food, materials, chemicals and energy are general drivers behind finding sustainable solutions for chemicals production. The depletion of fossil reserves and climate change issues make it necessary to find alternatives for the production of organic chemicals. Biomass has been proposed as a promising solution to both problems. However, this also raises questions on environmental compatibility and sustainability as noted in previous sections. The carbon efficiency of biorefinery technologies, sustainable use of resources and uncertainties of GHG emissions in feedstock supply chains are limiting factors that need careful assessment before a large scale biorefinery operation for the production of chemicals can be labeled as a sustainable solution to replace the fossil petrochemical route.

The viability of chemicals produced in biorefinery chains compared to the traditional petroleum refinery pathway to produce the same energy content and added value products will highly depend on the overall economic, social and environmental impact of the new biorefineries. General guidelines for how to make a case-specific interpretation of sustainability are missing. One reason for this is a lack of knowledge and/or consensus on how to describe and assess impacts of land and water use, e.g. on ecosystem services, different types of resource depletion and social impacts (Clancy et al., 2013). Climate impact and resource depletion are issues that cannot be omitted, especially if in the long run biomass becomes a limited resource. Embodied energy demand, water demand, carbon footprint and land use changes are among key indicators that define the sustainability of biorefineries.

The multitude of methodologies, methods and units currently used in evaluating GHG emissions are an obstacle in obtaining

Table 4
Comparison of pyrolysis and hydrothermal liquefaction (HTL).

Parameter	Pyrolysis	HTL
Operation temp.	300–750 °C	200–500 °C, opt 340 °C
Operation pressure	Atmospheric	2–25 MPa
Residence time	A few seconds	30 min
Feedstock requirements	Feed as dry as possible	Feed moisture content up to 65%
Main product yield	Bio-oil up to 75% Pyrolysis gas: 13–25%	Bio-oil up to 67%
Energy content of main product	Bio-oil: 30.7–41 MJ/kg Pyrolysis gas: 1.2–4.8 MJ/kg	Bio-oil: 30–39 MJ/kg HTL gas: 21 MJ/kg
Co-products	Syngas and Bio char	Methane (6–20%)
Recyclable waste	Fluidizing gas can be recycled to pyrolysis reactor.	Aqueous co-product can be used as feed to microalgae culture

uniform metrics for the sustainability assessment of final products. Future biorefineries need common criteria for sustainability and comprehensive LCA methodology. The assessment of chemicals produced from biomass seems to be practically absent in LCAs, although many publications show platform chemicals and a variety of other chemicals derived from them. The scaling up, carbon efficiency, and the economics of biorefinery production chains are all issues that need considerable future research and engineering effort for fully realizing the potential of the valuable resource stock of biomass in the production of bulk and high-value niche chemicals. The logistics of harvesting, intermediate storage and pretreatment of biomass resources need cost effective and sustainable arrangements.

7. Conclusions

The possibilities to reduce GHG emissions in biorefinery production chains are numerous. The GHG emissions in biofuel and bioenergy production chains have been extensively studied. In contrast, few studies have focused on the GHG emissions of other chemicals derived from biomass. The low carbon efficiency of fermentation technologies, and high CO_2 stack emissions from gasification + FT technology, require solutions. Widening the biorefinery production chains to include new emerging technologies could be an option. This paper makes an attempt to summarize pathways to decrease GHG emissions of biorefinery production chains through a climate impact management matrix, and highlights new emerging technologies of pyrolysis and hydrothermal liquefaction with a potential to improve the carbon efficiency and reduce GHG emissions in biorefinery chains.

The correct assessment of GHG emissions needs common criteria for sustainability and a comprehensive life cycle assessment (LCA) methodology. A set of functional units and equations is proposed for the evaluation of GHG emissions in a biorefinery value chain.

Uncertainties in assessing GHG emissions, especially of cultivated biomass resources, and land use restrictions support the widening of the resource base towards lignocellulosic biomass, wastes and algae. Sustainable development of commercial biorefineries will depend on the access to resources that do not compete with food production, and on the possibilities to increase carbon efficiency of the production chain. Responsible production of biobased chemicals has the potential to replace the fossil resources and slow down the net increases of GHG emissions through a 'short-cycle carbon system' of renewable bioresources.

Acknowledgments

The author is most grateful to M. Hurme, V. Alopaeus and H. Sixta, of Aalto University, Finland, for valuable discussions. A special thanks goes to the anonymous reviewers whose guiding remarks greatly improved the focus of this paper.

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